

PATENT ABSTRACTS OF JAPAN

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(54) ROOM TEMPERATURE CURING COMPOSITION

(57)Abstract:

PURPOSE: To obtain the subject composition, containing a specific silicon- containing polymer, a filler and a solid catalyst, excellent in fluidity and elongation and strength of a cured product and useful as sealing materials, adhesives, etc.

CONSTITUTION: This composition contains (A) an organic polymer composed of a polyoxyalkylene, obtained by polymerizing an alkylene oxide such as a 2-4C alkylene oxide with an initiator having 23 hydroxyl groups in one molecule using a composite metallic cyanide complex such as zinc hexacyanocobaltate as a catalyst and having 25000 number-average molecular weight and further ≥ 0.3 silicon-containing group expressed by the formula SiXaR13-a [R1 is a 1-20C (substituted) monovalent hydrocarbon group; X is a hydrolyzable group; (a) is 1-3] based on one molecule on the average of the whole molecule, (B) a filler such as silica or carbon black and (C) a curing catalyst such as dibutyltin dilaurate. Furthermore, the component (C) is used in an amount of preferably 0.001-10 pts.wt., especially 0.01-5 pts.wt. based on 100 pts.wt. component (A).

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CLAIMS

[Claim(s)]
 [Claim 1] A main chain makes a composite metal cyanide complex (D) a catalyst, and it consists of a with a number average molecular weights of 5000 or more produced by polymerizing alkylene oxide as an initiator (E) which has three hydroxyl groups even if small per molal polyoxyalkylene polymer (F). A room-temperature-curing nature constituent which becomes considering an organic compound (A), a buling agent (B), and a curing catalyst (C) which have a silicon content group from the following general formula (1) by a total of 0.3 or more molecule averages per monad as the main ingredients.



(R in formula is a univalent hydrocarbon group substitution of the carbon numbers 1-20, or

unsubstituted) X is a hydrolytic basis, a is 1, 2, or 3.

[Claim 2] A room-temperature-curing nature constituent of Claim 1 which is a complex in which a composite metal cyanide complex (D) uses zinc hexa cyanocobaltate as the main ingredients.

[Claim 3] A room-temperature-curing nature constituent of Claim 1 which is at least one sort as which alkylene oxide is chosen from ethylene oxide, propylene oxide, and butylene oxide.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001] [Industrial Application] This invention relates to the room-temperature-curing nature constituent hardened under hyposcopic-surface-moisture existence.

[0002] [Description of the Prior Art] The method of using it for a sealing material, adhesives, etc. using the hardening reaction of various kinds of compounds which have a hydrolytic silicon group at the end which is known as conventional, for example, modified silicone, system resin is known well, and is a useful method industrially.

[0003] It is desirable to have viscosity moderate at the time of combination and use, and in order for these to make the rubber elasticity which is rich in the dynamic characteristic of a hardened material, especially pliability reveal further, it is desirable to have a fixed molecular weight.

[0004] [Problem(s) to be Solved by the Invention] The publicly known polymer which has such an end hydrolytic silicon group is proposed by JP-S46-48191B, JP-S46-77553B, etc., for example. It is proposed by JP-S59-23002A etc. about the thing using the polyester compound of many organic compounds especially as a main component on these methods of introducing a hydrolytic silicon group after a polyfunctional hydroxyterminated compound, a vinyl ether compound of low molecular weight, setting it comparatively and carrying out Polymer Division quantification. That a reaction becomes a multi stage story, that a lot of salts carry out a byproduct, that molecular weight distribution (M_w/M_n) spreads considerably and becomes hypoviscosity considerably, and when it was going to make viscosity of a bulk of the elongation of a hardened material falling. Since bridge construction was easily built by forming many organic functions, it was difficult to obtain the polymer compound of the actually desirable amount of Polymer Division by this method.

[0005] [Means for Solving the Problem] This invention tends to cancel such a fault and a main chain makes a composite metal cyanide complex (D) a catalyst. It consists of a with a number average molecular weights of 5000 or more produced by polymerizing alkylene oxide in an initiator (E) which has three hydroxyl groups even if small per monad polyoxyalkylene polymer (F). It is going to provide a room-temperature-curing nature constituent which becomes considering an organic polymer (A), a building agent (B), and a curing catalyst (C) which have a silicon content group shown with the following formula (1) by a total of 0.3 or more molecule averages per monad as the main ingredients.



(R^1 in formula 1 is a univalent hydrocarbon group substitution of the carbon numbers 1-20, or unsubstituted). X is a hydrolytic base, i.e. 1, 2, or 3.

[0007] The polyoxyalkylene polymer (F) used as a main chain of an organic polymer (A) in this invention, a building agent (B) and a curing catalyst (C) which makes a composite metal cyanide complex (D) a catalyst, monohydroxy acid react to initiators, such as a hydroxy compound which has three hydroxyl groups even if small per monad, and manufactures is preferred.

[0008] By using a composite metal cyanide complex (D), M_w/M_n is narrower than a polyoxyalkylene polymer manufactured using the conventional alkaline metal catalyst. It is the amount of Polymer Division more, and it is possible to obtain a polyoxyalkylene polymer (F) of hypoviscosity more. Although a functional group number of a polyoxyalkylene polymer (F) can be arbitrarily controlled with the number of hydroxyl groups of an initiator (E) to a still more desirable thing, when a molecular weight is made equivalent, viscosity becomes low, so that it is many organic functions.

[0009] It is not based on a functional group number of a polyoxyalkylene polymer (F), but the physical properties of a cured body after combination of an organic polymer (A) can be freely controlled by content of a silicon content group. Therefore, physical properties, such as intensity and elongation, are the same, and a constituent using an organic polymer (A) of hypoviscosity can be obtained. Although the number of hydroxyl groups per monad of an initiator (E) used for this invention is three or more, it is preferred that they are 3-5 pieces from balance of physical properties, such as these viscosity, intensity, and elongation.

[0010] A compound which uses zinc hexa cyanocobaltate as the main ingredients as a composite metal cyanide complex (D) is preferred, and the solvent of the metal cyanide complex are preferred. The presentation can be made in a form of a solid, and the solid is easily isolated to JP-S46-27250B. As other, glyne, a lig. tin, cobalt, and glyne is especially preferred from handling at the time of manufacture of a compound, and tributanol indicated to JP-H4-14123A as alcohol is preferred.

[0011] As a polyoxyalkylene polymer (F), a polyoxyethylene compound, a polyoxypropylene compound, a polyoxy butylene compound, a polyoxy hexylene compound, polyoxy tetramethylene compounds, and/or these copolymers are mentioned. Especially desirable polyoxyalkylene polymers are polyoxypropylene triol and polyoxypropylene tetraol.

[0012] (1) is a general formula (1) is a univalent organic group substitution of the carbon numbers 1-20, or unsubstituted, and are a with a carbon number of eight or less alkyl group, a phenyl group, a propenyl, a fluoro alkyl group preferably. They are a methyl group, an ethyl group, a propyl group, a propenyl, a butyl group, a hexyl group, a cyclohexyl group, a phenyl group, etc. especially preferably. [0013] X in a general formula (1) is a hydrolytic base, for example, there are a halogen atom, an alkoxo group, an acyloxy group, an amide group, an amino group, an aminoxo group, a KETOKISHI mate group, an acid-amide group, a hydride group, etc. As for a carbon number of a hydrolytic base which has a carbon atom among these, six or less are preferred, and four especially or less are preferred. The desirable hydrolytic base can illustrate a with a carbon number of four or less lower alkoxo group especially a methoxy group and an ethoxy base, a propoxy group, a propenyl group, etc. [0014] In a general formula (1) is 1, 2, or 3, and it is preferred that it is especially 2 or 3.

[0015] Next, a manufacturing method of an organic polymer (A) is explained. As for an organic polymer (A) in this invention, what introduces a silicon content group into an end of a polyoxyalkylene polymer (F) which has a functional group so that it may state below, and is manufactured in preference. Such a compound is liquefied at a room temperature, and when a hardened material from a catalyst, it is provided with uses for a sealing material, adhesives, etc. also at low temperature comparatively, it is provided with the desirable characteristic.

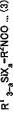
[0016] The method to which a hydrolytic compound expressed with an end of a polyoxyalkylene compound which has a functional group by what introduced an olefin group, and a general formula (2) is made to react.



(R^1 in formula 2, X, and R are the same as the above.)

As a method of introducing an olefin group here, A compound which has an unsaturation group and a functional group is made to react to terminal hydroxyl groups of a polyoxyalkylene compound. How to combine by other bond, ester bond, a urethane bond, carbonate combination, etc. Or when polymerizing alkylene oxide, a method of introducing an olefin group into a side chain, etc. are mentioned by adding and carrying out copolymerization of the olefin group content epoxy compounds, such as allyl glycid ether.

[0017] (4*) A method to which a compound expressed with an end of a polyoxyalkylene compound which has a functional group by a general formula (3) is made to react.



(R^1 in formula 1, X , and a are the same as the above.) R^2 is a divalent hydrocarbon group of the carbon numbers 1-17.

[0018] (e) A method to which W is a silicon compound expressed with a general formula (4) to this isocyanate group is made to react after making polyisocyanate compounds, such as tolylene diisocyanate, react to an end of a polyoxyalkylene compound which has a functional group and considering it as an isocyanate group end.



(R^1 in formula 1, R^2 , X , and a are the same as the above.) Active hydrogen containing group as which W was chosen from a hydroxy group, a carboxy group, a sulfinyl group, and an amino group (the 1st class or the 2nd class).

[0019] (e) A method which introduces an olefin group into an end of a polyoxyalkylene compound which has a functional group and to which the olefin group and an isocyanate group are made to react.

[0020] (e) A method to which W is a silicon compound expressed with a general formula (4) to this isocyanate group is made to react.

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uses the example of manufacture of an organic polymer (A) for the next by the reference examples 1-2, and is used for a comparative example by the reference examples 3-4 as shown first.

[0020] [Reference example 1] By a method given in JP-H5-72521A, propylene oxide is polymerized with a zinc hexa cyanocobaltate dimes complex by using the glyoxyl propylene oxide addition of the molecular weight 1000 as an initiator. Polypropylene (tri) of the number average molecular weight 2000 was obtained. Terminal hydroxyl group is changed into allyl ether groups, the addition reaction of the methyl dimethoxysilane was further carried out by having made chloroplatinic acid into the catalyst, and the organic polymer (P1) which has an average of 1.3 hydrolytic silicon groups per molecule was obtained.

[0021] [Reference example 2] By a method given in JP-H5-72521A, propylene oxide is polymerized with a zinc hexa cyanocobaltate dimes complex by using hexamethylsilane as an initiator. Polypropylene (tri) of the number average molecular weight 2000 was obtained. Terminal hydroxyl groups is changed into allyl ether groups, the addition reaction of the methyl dimethoxysilane was further carried out by having made chloroplatinic acid into the catalyst, and the organic polymer (P2) which has an average of 1.1 hydrolytic silicon groups per molecule was obtained.

[0022] [Reference example 3] By a method given in JP-H5-72521A, propylene oxide is polymerized with a zinc hexa cyanocobaltate dimes complex by using the diethylene glycol propylene oxide addition of the molecular weight 1000 as an initiator. Polypropylene (tri) of the number average molecular weight 2000 was obtained. Terminal hydroxyl group is changed into allyl ether groups, the addition reaction of the methyl dimethoxysilane was further carried out by having made chloroplatinic acid into the catalyst, and the organic polymer (P3) which has an average of 1.4 hydrolytic silicon groups per molecule was obtained.

[0023] [Reference example 4] Polypropylene (tri) of the number average molecular weight 3000 is made to react to tri(chlorophenyl) benzene by the method of a description at JP-530-123833. After making terminal hydroxyl groups react to allylchloride furthermore and considering it as end allyl ether groups, the addition reaction of the methyl dimethoxysilane was further carried out by having made chloroplatinic acid into the catalyst, and the organic polymer (P4) was obtained. The number average molecular weight of the organic polymer was 800.

[0024] [Working example 1 and 2 and comparative examples 1-3] As opposed to organic polymer (P1-P3) 100 weight section (100 weight) by method given in JP-H5-72521A, calcium carbonate 160 weight, hydroxy acid 20 weight, castor oil 5 weight, dicumyl phosphite 80 weight section. After adding and kneading, the organic polymer (P5) of the number average molecular weight 1000 was obtained. The organic polymer (P5) was obtained. The number average molecular weight of the organic polymer was 800.

[0025] [Working example 3] By a method given in JP-H5-72521A, propylene oxide is polymerized with a zinc hexa cyanocobaltate dimes complex by using the diethylene glycol propylene oxide addition of the molecular weight 1000 as an initiator. Polypropylene (tri) of the number average molecular weight 2000 was obtained. Terminal hydroxyl group is changed into allyl ether groups, the addition reaction of the methyl dimethoxysilane was further carried out by having made chloroplatinic acid into the catalyst, and the organic polymer (P6) which has an average of 1.4 hydrolytic silicon groups per molecule was obtained.

[0026] [Reference example 5] Polypropylene (tri) of the number average molecular weight 3000 is made to react to tri(chlorophenyl) benzene by the method of a description at JP-530-123833. After making terminal hydroxyl groups react to allylchloride furthermore and considering it as end allyl ether groups, the addition reaction of the methyl dimethoxysilane was further carried out by having made chloroplatinic acid into the catalyst, and the organic polymer (P7) was obtained. The number average molecular weight of the organic polymer was 800.

[0027] [Working example 6] By a method given in JP-H5-72521A, propylene oxide is polymerized with a zinc hexa cyanocobaltate dimes complex by using the diethylene glycol propylene oxide addition of the molecular weight 1000 as an initiator. Polypropylene (tri) of the number average molecular weight 2000 was obtained. Terminal hydroxyl group is changed into allyl ether groups, the addition reaction of the methyl dimethoxysilane was further carried out by having made chloroplatinic acid into the catalyst, and the organic polymer (P8) which has an average of 1.4 hydrolytic silicon groups per molecule was obtained.

[0028] [Reference example 7] Polypropylene (tri) of the number average molecular weight 3000 is made to react to tri(chlorophenyl) benzene by the method of a description at JP-530-123833. After making terminal hydroxyl groups react to allylchloride furthermore and considering it as end allyl ether groups, the addition reaction of the methyl dimethoxysilane was further carried out by having made chloroplatinic acid into the catalyst, and the organic polymer (P9) was obtained. The number average molecular weight of the organic polymer was 800.

[0029] [Working example 8] By a method given in JP-H5-72521A, propylene oxide is polymerized with a zinc hexa cyanocobaltate dimes complex by using the diethylene glycol propylene oxide addition of the molecular weight 1000 as an initiator. Polypropylene (tri) of the number average molecular weight 2000 was obtained. Terminal hydroxyl group is changed into allyl ether groups, the addition reaction of the methyl dimethoxysilane was further carried out by having made chloroplatinic acid into the catalyst, and the organic polymer (P10) which has an average of 1.4 hydrolytic silicon groups per molecule was obtained.

[0030] [Reference example 9] Polypropylene (tri) of the number average molecular weight 3000 is made to react to tri(chlorophenyl) benzene by the method of a description at JP-530-123833. After making terminal hydroxyl groups react to allylchloride furthermore and considering it as end allyl ether groups, the addition reaction of the methyl dimethoxysilane was further carried out by having made chloroplatinic acid into the catalyst, and the organic polymer (P11) was obtained. The number average molecular weight of the organic polymer was 800.

[0031] [Working example 10] By a method given in JP-H5-72521A, propylene oxide is polymerized with a zinc hexa cyanocobaltate dimes complex by using the diethylene glycol propylene oxide addition of the molecular weight 1000 as an initiator. Polypropylene (tri) of the number average molecular weight 2000 was obtained. Terminal hydroxyl group is changed into allyl ether groups, the addition reaction of the methyl dimethoxysilane was further carried out by having made chloroplatinic acid into the catalyst, and the organic polymer (P12) which has an average of 1.4 hydrolytic silicon groups per molecule was obtained.

[0032] [Reference example 11] Polypropylene (tri) of the number average molecular weight 3000 is made to react to tri(chlorophenyl) benzene by the method of a description at JP-530-123833. After making terminal hydroxyl groups react to allylchloride furthermore and considering it as end allyl ether groups, the addition reaction of the methyl dimethoxysilane was further carried out by having made chloroplatinic acid into the catalyst, and the organic polymer (P13) was obtained. The number average molecular weight of the organic polymer was 800.

[0033] [Working example 12] By a method given in JP-H5-72521A, propylene oxide is polymerized with a zinc hexa cyanocobaltate dimes complex by using the diethylene glycol propylene oxide addition of the molecular weight 1000 as an initiator. Polypropylene (tri) of the number average molecular weight 2000 was obtained. Terminal hydroxyl group is changed into allyl ether groups, the addition reaction of the methyl dimethoxysilane was further carried out by having made chloroplatinic acid into the catalyst, and the organic polymer (P14) which has an average of 1.4 hydrolytic silicon groups per molecule was obtained.

[0034] [Reference example 13] Polypropylene (tri) of the number average molecular weight 3000 is made to react to tri(chlorophenyl) benzene by the method of a description at JP-530-123833. After making terminal hydroxyl groups react to allylchloride furthermore and considering it as end allyl ether groups, the addition reaction of the methyl dimethoxysilane was further carried out by having made chloroplatinic acid into the catalyst, and the organic polymer (P15) was obtained. The number average molecular weight of the organic polymer was 800.

[0035] [Working example 14] By a method given in JP-H5-72521A, propylene oxide is polymerized with a zinc hexa cyanocobaltate dimes complex by using the diethylene glycol propylene oxide addition of the molecular weight 1000 as an initiator. Polypropylene (tri) of the number average molecular weight 2000 was obtained. Terminal hydroxyl group is changed into allyl ether groups, the addition reaction of the methyl dimethoxysilane was further carried out by having made chloroplatinic acid into the catalyst, and the organic polymer (P16) which has an average of 1.4 hydrolytic silicon groups per molecule was obtained.

[0036] [Reference example 15] Polypropylene (tri) of the number average molecular weight 3000 is made to react to tri(chlorophenyl) benzene by the method of a description at JP-530-123833. After making terminal hydroxyl groups react to allylchloride furthermore and considering it as end allyl ether groups, the addition reaction of the methyl dimethoxysilane was further carried out by having made chloroplatinic acid into the catalyst, and the organic polymer (P17) was obtained. The number average molecular weight of the organic polymer was 800.

[0037] [Working example 16] By a method given in JP-H5-72521A, propylene oxide is polymerized with a zinc hexa cyanocobaltate dimes complex by using the diethylene glycol propylene oxide addition of the molecular weight 1000 as an initiator. Polypropylene (tri) of the number average molecular weight 2000 was obtained. Terminal hydroxyl group is changed into allyl ether groups, the addition reaction of the methyl dimethoxysilane was further carried out by having made chloroplatinic acid into the catalyst, and the organic polymer (P18) which has an average of 1.4 hydrolytic silicon groups per molecule was obtained.

[Table 1]

No.	試験例1		試験例2		比較例1	
	P1	P2	P2	P3	P3	P3
有機重合体	1.2	1.1	1.1	1.1	1.1	1.1
M_n	5.2	4.9	5.4	5.4	5.4	5.4
数均分子量	7.20	6.80	7.50	7.50	7.50	7.50
重量平均分子量	11000	8500	15000	15000	15000	15000

[0038] [Comparative example 2] The viscosity of the organic polymer (P4) compounded by the reference example 4 was 20000 cps (a measuring condition is the same as the above).

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http://www.lipid.lipid.go.jp/cgi-bin/tran_web.cgi?ataw=HtUp3A3ZF2Fvww4.pdf... 2010/08/05

[0038]

[Effect of the Invention] Use the composite metal cyanide complex catalyst of this invention, and have intrinsically the polyoxallylene polymer produced by polymerizing allylene oxide in the initiator which has three or more hydroxyl groups in a main chain. The room-temperature-curing nature constituent which uses a hydrolytic silicon group content organically polymer as a hardening component has the effect of having the outstanding elongation and strength properties, and low viscosity as compared with the polymer which carries out chain extension of the polymer of comparatively a low number average molecular weight known conventionally, and manufactures it

[Translation done.]